

Use of partially saponified vinyl ester polymers in hot-melt adhesive compositions

5 The invention relates to the use of partially saponified vinyl ester homopolymers and copolymers in hot-melt adhesive compositions.

Hot-melt adhesives (hotmelts) are used in the packaging sector, among others, as adhesives: for example, as 10 adhesives for paper, paperboard, cardboard, and wood. Common hot-melt adhesives are based on ethylene-ethyl acrylate copolymers, polyamides, and ethylene-vinyl acetate copolymers. In train with the increasing recycling of packaging materials there is a need for 15 the adhesives to be readily detachable from the packaging materials. Ideally they ought to be amenable to removal by washing with water. The abovementioned standard hotmelts do not meet this condition.

20 JP-A 2001-220563 discloses a water-soluble or water-dispersible hot-melt adhesive composition which comprises polyvinyl alcohol having a degree of polymerization of \leq 350 and a degree of hydrolysis of \leq 80 mol%, mannitol, and polypropylene glycol. A 25 disadvantage there is the tendency to gel under long-term temperature exposure, owing to the high viscosity. JP-A 62-043477 describes a hot-melt adhesive based on a polyvinyl alcohol having a degree of polymerization of preferably 100 to 1500 and a degree of hydrolysis of 20 to 95 mol%, the vinyl alcohol units being arranged in blocks. JP-A 2003-003140 describes hot-melt adhesives 30 comprising a polyvinyl alcohol (degree of hydrolysis $<$ 60 mol%), an anionic emulsifier, and plasticizer. Owing to the anionic emulsifier the water resistance of 35 the bond is unsatisfactory. A disadvantage of these hot-melt adhesives is their low bond strength, excessively high price, excessively high melt viscosity, and the associated tendency to gel.

It was an object of the invention to develop a hot-melt adhesive composition which exhibits good fluidity, leads to stable bonds, but is readily removable with water from the material to which sticking was intended.

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The invention provides for the use of partially saponified vinyl ester homopolymers and copolymers in hot-melt adhesive compositions, characterized in that the vinyl ester homopolymers and copolymers have a molecular weight $M_w < 70000$ and the partially saponified vinyl ester homopolymers and copolymers have a degree of hydrolysis of 62 to 86 mol%, and the hot-melt adhesive composition contains no mannitol.

10 15 Suitable partially saponified vinyl ester homopolymers and copolymers are partially saponified vinyl ester polymers having a degree of hydrolysis of 62 to 86 mol%, preferably 65 to 75 mol%, most preferably 70 mol%. The weight-average molecular weight M_w is < 70000, preferably 5000 to 30000 (determined by means of gel permeation chromatography), the molecular weight being determined prior to the saponification and the molecular weight M_w therefore referring to the as yet unsaponified vinyl ester homopolymer or copolymer. The 20 25 hot-melt adhesive composition contains no anionic emulsifiers. In the partially saponified vinyl ester homopolymers and copolymers the vinyl alcohol units are randomly distributed.

30 35 Suitable vinyl esters are vinyl esters of unbranched or branched carboxylic acids having 1 to 18 carbon atoms. Preferred vinyl esters are vinyl acetate, 1-methylvinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, vinyl pivalate, and vinyl esters of α -branched monocarboxylic acids having 5 to 13 carbon atoms, examples being VeoVa9^R or VeoVa10^R (tradenames of Resolution Performance Products), and also mixtures thereof. Vinyl acetate is particularly preferred.

Besides the vinyl ester units it is also possible where appropriate for one or more monomers to be copolymerized from the group encompassing methacrylic esters and acrylic esters of alcohols having 1 to 15 carbon atoms, olefins, dienes, vinyl aromatics, ethylenically unsaturated monocarboxylic and dicarboxylic acids, and vinyl halides. Suitable monomers from the group of the esters of acrylic acid or methacrylic acid are methyl acrylate, methyl methacrylate, n-, iso-, and tert-butyl acrylate, 2-ethylhexyl acrylate, and norbornyl acrylate. Suitable dienes are 1,3-butadiene and isoprene. Examples of polymerizable olefins are ethene and propene. Vinyl aromatics which can be copolymerized are styrene and vinyltoluene. Examples of suitable monocarboxylic and dicarboxylic acids are acrylic acid, methacrylic acid, crotonic acid, and fumaric acid. From the group of the vinyl halides it is common to use vinyl chloride. Most preference is given to ethylene, crotonic acid, and vinyl chloride. The fraction of these comonomers is calculated such that the fraction of vinyl ester monomer is > 50 mol% in the vinyl ester polymer.

25 Maximum preference is given to partially saponified vinyl acetate homopolymers, partially saponified vinyl acetate-vinyl laurate copolymers, vinyl acetate-crotonic acid copolymers, and mixtures thereof.

30 The partially saponified vinyl ester homopolymers and copolymers can be prepared in a known way from the corresponding vinyl ester polymers by means of saponification (hydrolysis). The vinyl ester polymers are prepared in a known way preferably by bulk polymerization, suspension polymerization or by polymerization in organic solvents, with particular preference in alcoholic solution. The polymerization is carried out under reflux at a temperature of 55°C to 100°C and initiated free-radically by addition of

commonplace initiators.

The saponification of the vinyl ester polymers takes place in a manner known per se by for example the belt 5 or extruder method or in a stirred tank, in the alkaline or acidic range with addition of acid or base. Preferably the solid vinyl ester resin is taken up in alcohol, methanol for example, to set a solids content of 15% to 70% by weight. The hydrolysis is preferably 10 carried out in the basic range, by addition of NaOH, KOH or NaOCH₃, for example. The base is used generally in an amount of 1 to 5 mol% per mole of ester units. The hydrolysis is carried out at temperatures from 30°C 15 to 70°C. After the end of the hydrolysis the solvent is removed by distillation. Alternatively the polyvinyl alcohol can be obtained as an aqueous solution by successive addition of water while the solvent is distilled off.

20 The hot-melt adhesive composition may further comprise 0 to 50% by weight, preferably 15% to 50% by weight, of sorbitol, based in each case on the total weight of the hot-melt adhesive composition. This addition reduces 25 the melt viscosity and enhances the flexibility of the adhesive bond and the adhesion to different substrates.

To reduce the surface tension and the viscosity of the melt it is possible further to admix the hot-melt adhesive composition with waxes, such as hydrocarbon 30 waxes, polyethylene waxes, and polyamide waxes, for example. Preference is given to polyamide waxes such as ethylenebisstearamide wax. The amount used is preferably 0.1% to 15% by weight, based on the total weight of the hot-melt adhesive composition.

35 Suitable additives for improving the compatibility of the individual components of the hot-melt adhesive composition are fatty acid esters such as glycerol monostearate and glycerol distearate, which where

appropriate are used in a weight ratio of 0.1 : 1 to 1 : 1 with respect to the wax fraction of the hot-melt adhesive composition.

5 Where appropriate it is also possible for water-soluble plasticizers to be included, such as glycerol esters of rosin, methyl esters of rosin, pentaerythritol esters of rosin, and polyalkylene glycols, preferably polypropylene glycol. The amounts in the hot-melt adhesive composition are 0 to 10% by weight, preferably 1% to 5% by weight, based on the overall weight of the hot-melt adhesive composition.

15 Examples of further additives include antioxidants for increasing the gelling stability, based on corresponding phosphites, sterically hindered phenols, lactones or mixtures thereof. Antioxidants of this kind are available commercially and are employed where appropriate in an amount of up to 2% by weight, based 20 on the overall weight of the hot-melt adhesive composition.

25 The hot-melt adhesive composition is suitable for use as adhesive for paper, paperboard, cardboard, wood, and plastic, especially as a label adhesive for PET containers. The hot-melt adhesive composition is distinguished over the prior art by virtue of the fact that the adhesive is water-soluble and yet remains thermoplastically processible, and the adhesive is 30 readily amenable to removal by washing when substrates bonded using it are recycled.

35 The examples which follow serve for further illustration of the invention:

The formulas specified in Table 1 were tested:

Solid resin: partially saponified polyvinyl acetate with degree of hydrolysis = 70 mol% and

molecular weight Mw (PVAc) = 10000
PPG 400: polypropylene glycol with OH number of 400
Licolub: ethylenebisstearamide wax
5 Tegomuls: glycerol monostearate

Table 1:

Example	C1	2	3	4	5	6	7
Solid resin [g]	60	96	75	70.3	66.0	87.5	81.0
Sorbitol [g]			21	19.7	18.5		
Mannitol [g]	36						
PPG 400 [g]	4.0	4.0	4.0	3.8	3.5	4.7	4.3
Licolub [g]				5.0	8.0	6.2	9.8
Tegomuls [g]				1.3	4.0	1.6	4.9

10 The specified formulas were used to conduct the following test, whose results are summarized in Table 2:

Determination of melt viscosity [Pas]:

15 The melt viscosity was determined by measuring the hot-melt adhesives using a high-temperature rheometer from Bohlin and plotting the rheology curves in the temperature range 100°C to 180°C (gap distance 500 µm, frequency 1 Hz, Def 0.05, temperature ramp 5°C/min, 20 oscillating measurement).

Determination of water solubility [s]:

The water-solubility was determined by sealing 2 cotton strips (1 cm x 4 cm) with the corresponding formulation 25 at 180°C. The sealed bond was immersed in a waterbath at room temperature and loaded with a weight of 10 g. A measurement was made of the time until the bond had undergone complete parting.

Table 2:

Example	C1	2	3	4	5	6	7
Viscosity at 120°C [Pas]	1410	2610	612	1000	942	333	622
H ₂ O solubility [s]	245	107	366	170	214	250	280

5 Discussion of results:

In comparison to the prior art formulation the inventive formulations combine generally much-improved flow behavior with adhesive films that exhibit comparable water-solubility.